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SURFACTANT INDUCED MESOMORPHIC BEHAVIOUR OF FLEXIBLE POLYMERS

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Abstract: Conditions for micro phase separated structures based on flexible polymers associated with surfactants have been investigated. Reasonably strong attractive interactions are required to oppose macro phase separation between polymer and surfactant. In order to obtain micro phase separation, additionally a sufficiently strong polar-nonpolar repulsion has to be present. Poly(4-vinyl pyridine), poly(2-vinyl pyridine) and polyamide 6 have been used as model polymers in this work. Associations based on protonation, metal coordination and hydrogen bonding are presented and shown to yield micro phase separation under suitable conditions. In the charged systems, the polar-nonpolar repulsion easily becomes large enough to render micro phase separated structures. In hydrogen bonded (i.e. noncharged) systems a more delicate balance can be achieved in which case an order-disorder transition takes place from a homogeneous state, exhibiting nonetheless a distinct SAXS peak due to characteristic block copolymer-like fluctuations, to a micro phase separated ordered state.

INTRODUCTION

Several previous observations illustrated that interesting self organization, phase transitions and conformational behaviour can be observed for flexible polymers associated with surfactants in bulk and in solution. In *aqueous solutions* surfactants are known to undergo self organization into structures including spherical and cylindrical micelles, inverted micelles, bilayer sheets and vesicles. This hydrophobic effect extends to aqueous polymer-surfactant systems, such as poly(ethylene oxide)-sodium dodecyl sulphate-water (for a recent results, see Ref. 1).

Polymer-surfactant complexes have recently been developed also for electrically conducting polymers. In this case the polymer chains are usually rigid or semi-rigid. Mesomorphic structures of alkylsulphonates of polypyrrole have been observed (Ref. 2). Polyaniline (PANI), which is infusible and poorly soluble in common solvents, can be plasticized by surfactant-like dopands (Ref. 3), such as dodecyl benzene sulphonic acid (DBSA), to yield mesomorphic fusible complexes (Ref. 4).

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Mesomorphic structures based on flexible polymers associated with surfactants *in bulk* have recently been presented by us and others for polyelectrolyte-surfactant complexes (Refs. 5,6), poly(vinyl pyridine) complexed with surfactants due to metal coordination bonding (Ref. 7), polyacid-amine complexes (Ref. 8) and poly(vinyl pyridine) hydrogen bonded to *mesogenic* biphenyl derivatives (Ref. 9). In this work we demonstrate that systems consisting of flexible polymers complexed with surfactants with different strengths of association and repulsion allow a rich variety of self-organized structures and order-disorder transitions. We will review previously obtained results (Refs. 10,11,12), discussing these in terms of newly acquired information based on synchrotron X-ray scattering experiments, and present our most recent observations on more complicated systems involving multi-functional surfactants. As model polymers we have selected nitrogen containing polymers poly(4-vinyl pyridine), poly(2-vinyl pyridine) and polyamide 6 (i.e. P4VP, P2VP and PA6) because these allow experimentation with different types of interactions, such as protonation, metal coordination, and hydrogen bonding. In addition, the effect of charges on the mesomorphic state can be investigated.

EXPERIMENTAL

P4VP and P2VP were purchased from Polyscience Europe GmbH. The molar masses are M_V=49 000 $gmol^{-1}$ and 330 000 $gmol^{-1}$, respectively, as determined by viscometry. PA6 is of commercial quality Ultramid B3S by BASF. Surfactants have been purchased from Merck, Fluka and Tokyo Kasei and are of highest available purity. Zinc dodecyl benzene sulphonate, i.e. $Zn(DBS)_2$, has been synthesised from ZnO and DBSA, and the reaction has been checked with FTIR and WAXS (Ref. 7). The polymer-surfactant complexes have been prepared in solutions of ethanol, chloroform, DMF, or *m*-cresol, depending on the polymer and the surfactant. The amount of the surfactant has been denoted using molar basis: for example, $P4VP(PDP)_{0.85}$ means that there is 0.85 mol of *m*-pentadecyl phenol (PDP) relative to 1 mol of P4VP repeat units. The extent of complexation has been studied using FTIR. The self-organization has been investigated by SAXS, WAXS, calorimetry and polarizing microscopy. Both conventional and synchrotron X-ray sources (Daresbury Synchrotron Laboratory, UK) have been used for X-ray studies.

RESULTS AND DISCUSSION

General Considerations

The following examples demonstrate that, in order to achieve mesomorphic structures in polymer-surfactant systems, two essential conditions have to be met. The association between the polar end of the surfactant and the polymer has to be strong enough to prevent macro phase separation. But, strong association in itself is not sufficient. In addition, the repulsion between the polar moieties of the polymer-surfactant complex and the nonpolar alkyl tails has to be sufficiently large to induce

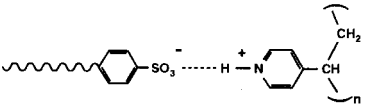
micro phase separation. The micro phase separated structures (resembling liquid crystalline or block copolymer structures) can be identified by small angle X-ray scattering in combination with birefringence in optical microscopy. This latter observation is essential, because even in a dynamical equilibrium situation between polymer and surfactant, a SAXS peak can be present in the homogeneous state as long as the association is strong enough.

Based on a large number of experiments, we have distinguished four different regimes of behaviour for polymer-surfactant systems:

I micro phase separated mesomorphic state
II homogeneous state exhibiting a distinct SAXS peak
III homogeneous state without a SAXS peak
IV macro phase separated state

Surfactants Capable of Proton Transfer

Due to the strong acidity of the sulphonic acid group, DBSA is able to transfer its acidic proton to the basic pyridine rings of P4VP and P2VP (see **1**). The resulting ionic interaction is strong, and manifests itself for P4VP as a large shift from 1597 cm^{-1} to 1637 cm^{-1} in the characteristic pyridine ring FTIR band due to formation of charged pyridinium ring (Ref. 6).

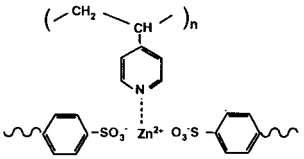


1

X-ray studies and birefringence show that a mesomorphic complex P4VP(DBSA)$_x$ is formed which is a polyelectrolyte due to the charges. Based on these data, we concluded that the structures are smectic with alternating polar and nonpolar layers, with long periods ranging from ca. 27 Å for x=0.5 (half complexed) to ca. 29 Å for x=1.0 (nominally fully complexed case). The influence of the amount of surfactant is small, however, which may be explained by assuming clustering of the surfactants at low degree of complexation. In this case the nearly fully complexed domains are imbedded in non-complexed P4VP medium and the small variation in long period may be attributed to domain size effects (Refs. 11,12). Due to the strong association (proton transfer) and strong polar-nonpolar repulsion (ionic charges), this system, and similar ones, belong to regime I at least to 200 °C.

Surfactants Capable of Coordination Bonding

Surfactants can be strongly associated with P4VP due to metal coordination, as is demonstrated by the large FTIR pyridine band shift from 1597 cm^{-1} to 1617 cm^{-1} (Ref. 7) upon complexation with $Zn(DBS)_2$ (see **2** where the possible bound water is not depicted for simplicity).



2

In addition, large nonpolar-polar repulsion is again present due to the charges. Therefore, a micro phase separated metallo-mesogenic complex P4VP(Zn(DBS)$_2$)$_x$ is obtained, which is stable to at least 200 °C. As before, the structure seems to be smectic, with a long period of 26.1 Å for x=0.25, increasing slightly to 27.8 Å for x=1.0 (Ref. 7). The long period behaves qualitatively similarly as in the case of DBSA, suggesting again clustering due to charge induced co-operative complexation. Not surprisingly, P4VP(Zn(DBS)$_2$)$_x$ and similar systems belong to Regime I as well.

Also PA6 forms mesogenic phases due to coordination with Zn(DBS)$_2$ as is illustrated in Fig. 1. This case differs slightly from the P4VP case due to the presence of the amide group in the main chain as compared to the basic nitrogen in the pyridine ring. The long period now slightly decreases from 28.0 Å at x=0.15 to 26.4 Å for x=1.0, compared to 25.4 Å for pure Zn(DBS)$_2$. Since, pure Zn(DBS)$_2$ forms a mesomorphic smectic structure as well, more interesting situations arise for less amphiphilic surfactants, in particular those that can form hydrogen bonds with P4VP.

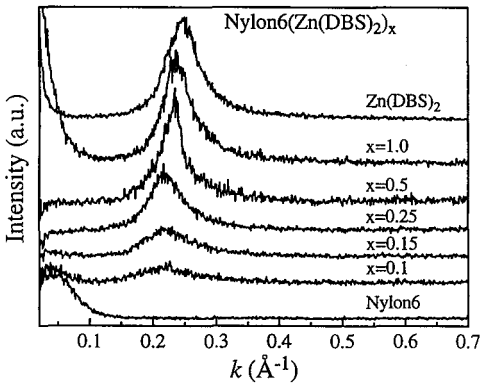


Fig. 1 SAXS data for PA6 complexed with Zn(DBS)$_2$ at different mole fractions x.

Phenolic Surfactants Capable of One Hydrogen Bonding

A model surfactant of this group is *m*-pentadecyl phenol (PDP), see **3**. According to FTIR, it yields only a small shift from 1597 cm^{-1} to 1603 cm^{-1} in the characteristic pyridine ring absorption upon complexation (Ref. 11). Complementary studies at bands 1415 and 993 cm^{-1} suggest that almost full complexation can be achieved (Ref. 11).

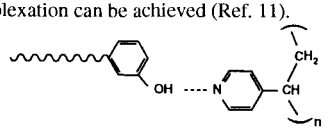


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Figure 2 shows time resolved SAXS data for P4VP(PDP)$_{0.85}$ during cooling from 100 °C to 0 °C Above ca. 63 °C the system is in regime II, i.e. in a homogeneous disordered state. A SAXS peak is, however, prominently present due to concentration fluctuations with a characteristic length scale determined by the hydrogen bonded comb-like structures. A first order order-disorder transition (ODT) to a microphase separated state takes place at ca. 63 °C.

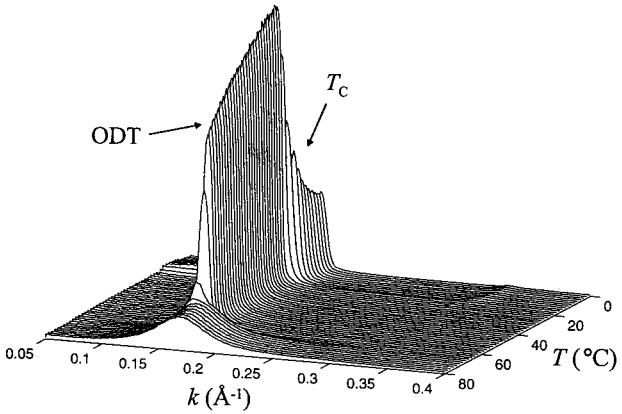


Fig. 2. Time resolved SAXS spectra of P4VP(PDP)$_{0.85}$ during cooling from 100 °C to 0°C.

This ordered phase is smectic with a long period of approximately 38 Å (regime I). Further cooling leads to crystallization of the side chains at ca. 20 °C (T_C). Both transitions are exothermic as demonstrated by DSC experiments presented in Figure 3.

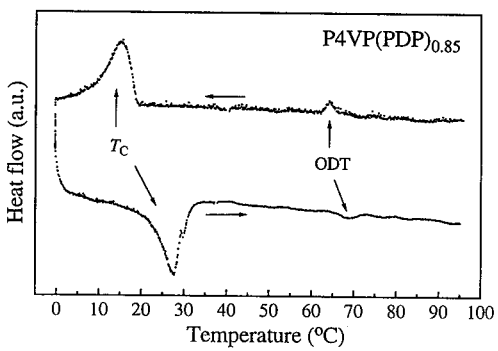


Fig. 3 DSC data for P4VP(PDP)$_{0.85}$ obtained during heating and cooling with 5 °C/min.

As a function of x, the long period decreases as 1/x.. The strong increase at low x-values is in complete contrast to the charged systems (see cases of P4VP with DBSA and Zn(DBS)$_2$). Simple considerations, assuming non-cooperative complexation, suggest that the increased long period at small x-values is due to an increased thickness of the polar layer (Ref. 12).

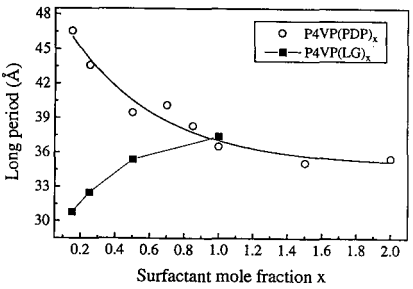


Fig. 4. Long period in the samples $P4VP(PDP)_X$ and $P4VP(LG)_X$ as a function of molar fraction of the surfactant.

There is a simple analogy with lamellar microemulsions consisting of water, oil, and surfactant layers, as is illustrated in Fig. 5. In our case the role of water is played by the polar P4VP polymer. Just as a higher volume fraction of water implies a larger long period, so does a higher volume fraction of P4VP. The same explanation also works for the PA6-$Zn(DBS)_2$ case.

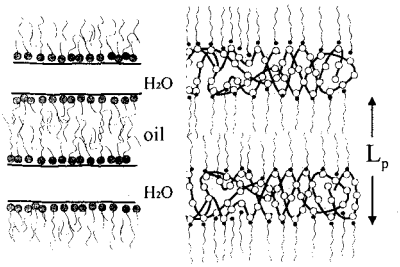
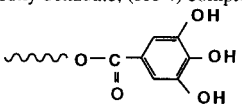


Fig. 5. Illustration of the analogy between polymer-surfactant systems and lamellar microemulsions

Phenolic Surfactants Capable of Several Hydrogen Bondings

A characteristic surfactant of this group is provided by lauryl gallate (LG), i.e. 1-dodecyl-3,4,5-trihydroxy benzoate, (see 4) complexed with P4VP.



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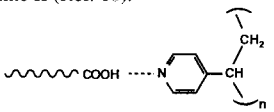
Mesomorphic behaviour is observed for $P4VP(LG)_X$ (Ref. 10). The long period is reduced for small x, i.e. at low degrees of complexation (Fig. 4). This observation is surprising in comparison with the corresponding $P4VP(PDP)_X$ complexes with only one hydroxyl group. At the moment we do not yet know the exact architecture of the multiple bondings. It is likely that LG physically crosslinks the neighbouring polymer chains and therefore this system may yield mesomorphic physically

crosslinked polymer-surfactant system. Although a careful timeresolved X-ray scattering investigation has not yet been performed, there are indications that the P4VP(LG)$_{1.0}$ undergoes an order-disorder transition around 80 °C.

Carboxylic Acid Surfactants Capable of Hydrogen Bonding

Complexes with dodecanoic acid ($C_{11}H_{23}COOH$), hexadecanoic acid ($C_{15}H_{31}COOH$) and nonadecanoic acid ($C_{18}H_{37}COOH$) were prepared with P4VP. In the case of carboxylic acids the strong tendency for crystallization and intermolecular association easily obscure interpretations unless proper care is exerted. At room temperature, where all of the above surfactants are in the crystalline state, FTIR suggests that 1 mol of dodecanoic acid mixed with 1 mol P4VP repeat units renders a split FTIR peak, suggesting only partial complexation. For hexadecanoic and nonadecanoic acids, no FTIR shifts were observed. These results indicate that carboxylic acids do not associate strongly with P4VP. Above the melting temperature of the surfactants, however, characteristic SAXS peaks are observed, but without a sign of birefringence. Therefore the carboxylic acid surfactants are in regime II (Ref. 10).



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Aliphatic Alcohol Surfactants Capable of Hydrogen Bonding

Dodecanol ($C_{12}H_{25}OH$) renders only partial complexation with P4VP based on FTIR shifts (1 mol dodecanol vs 1 mol of P4VP repeat units). No SAXS peaks are observed. Longer aliphatic alcohols macro phase separate. Therefore, dodecanol is a limiting case where the hydrogen bonding is still strong enough to compensate for the unfavourable alkyl-polymer interaction. However, the association is too weak to give rise to a SAXS peak; i.e. we are essentially not dealing with a self-associating system.Therefore, P4VP in combination with dodecanol belongs to regime III. For increasing alkyl tail lengths, the number of unfavourable interactions in the homogeneous state becomes too large and macro phase separation occurs, placing these systems in regime IV (Ref. 10).

CONCLUSIONS

Mesomorphic polymer/surfactant complexes have been discussed, based on different interactions such as protonation, coordination bonding and hydrogen bonding. Charged structures such as P4VP complexed with DBSA or Zn(DBS)$_2$ render micro phase separated structures due to strong association between the surfactant and the polymer in combination with strong repulsion between the

charged polar moieties and the nonpolar alkyl tails. Charge clustering effects are also suggested. Hydrogen bonded phenolic surfactants associated with P4VP such as pentadecyl phenol show more interesting phase behaviour. At high temperatures a homogeneous phase is observed with fluctuation induced SAXS peaks. Upon cooling, an order-disorder transition to micro phase separated state occurs. Further cooling yields side chain crystallization. Phenolic surfactants with several hydrogen bonding moieties also show mesomorphism, probably in combination with physical crosslinking. Limiting case hydrogen bonding surfactants have also been screened, leading only to miscibility without micro phase separation. The concepts can be extended to many other polymers. One example given is polyamide 6 complexed with $Zn(DBS)_2$, which is mesomorphic due to metal coordination .

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